

Low-Cost Manufacturing of Multi-Layer Ceramic Fuel Cells

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Objectives

- Develop low-cost manufacturing methods for planar SOFC elements with cathode-supported and anode-supported configurations.
- Evaluate the electrochemical performance of planar SOFC elements by single-cell and long-term testing.
- Correlate results of SOFC testing with compositional and morphological variations.
- Establish non-destructive testing methodologies as quality control tools during manufacture of planar SOFC elements.

Key Milestones

- Established tape casting, colloidal-spray deposition, screen-printing, and co-sintering methods for anode-supported planar SOFC elements.
- Established laser dilatometry and optical profilometry as non-destructive characterization tools for process development and quality control.
- Scaled-up fabrication of anode-supported cells to 100-cm² areas.
- Developed composite formulations for high-performance cathode materials, and established screen-printing method for depositing cathode coatings.

Approach

NexTech Materials is leading this collaborative project aimed at development of low-cost ceramic manufacturing processes for planar solid oxide fuel cell elements. Team members on this project include NexTech, University of Missouri-Rolla, Oak Ridge National Laboratory, Northwestern University, Gas Technology Institute, Ohio State University, Michael A. Cobb & Company, Advanced Materials Technologies, and the Edison Materials Technology Center.

NexTech Materials has developed a fabrication process for anode-supported planar SOFC elements, based on tape casting of anode (NiO/YSZ) substrates, colloidal spray deposition of the YSZ electrolyte films, co-sintering of the anode/YSZ bilayer elements, and screen printing of cathode layers. ORNL developed a similar fabrication process for anode-supported cells, except that YSZ films were deposited by screen printing prior to co-sintering. UMR's process development work focused on a novel spin-coating approach for depositing ultra-thin, nano-crystalline YSZ electrolyte films on pre-sintered cathode substrates. Specific fabrication challenges addressed included matching of shrinkages during co-sintering, controlling porosity and morphology of sintered electrode substrates, and maintaining required flatness of co-sintered elements. Laser dilatometry and optical profilometry methods were established at Ohio State University (OSU) to monitor sintering shrinkages and to characterize flatness and surface topology of sintered substrates and co-sintered elements.

Ongoing work in the project focuses on comprehensive characterization and testing of planar SOFC elements. This involves single-cell testing at Northwestern University to assess SOFC performance; long-term testing at GTI to assess performance of planar cells under application-specific conditions, non-destructive testing at Ohio State University using optical profilometry, and mechanical property testing of cells at Ohio State and Oak Ridge.

Results

NexTech's work involved development of a fabrication process for both anode-supported and cathode-supported planar elements. These processes included tape casting and lamination of cathode (LSM) and anode (NiO/YSZ) substrates, ultrasonic-spray deposition for YSZ electrolyte films, co-sintering methods for bi-layer substrates, and screen-printing of opposite electrodes (cathode or anode). ORNL's process development work focused on tape casting of NiO/YSZ anode substrates, screen printing of YSZ electrolyte films, co-sintering of anode/YSZ bilayer elements, and screen printing of cathode coatings. UMR developed tape casting and lamination methods for cathode substrates, and colloidal processing and spin-coating methods for nano-crystalline YSZ electrolyte films.

A key challenge associated with co-sintering of cathode-supported cells is the potential for adverse reactions between the cathode (LSM) substrate and the electrolyte (YSZ) film. For this reason, NexTech adapted a composite interlayer approach. The interlayer composition was designed to prevent adverse reactions between the LSM cathode substrate and the YSZ electrolyte films during co-sintering and to improve low-temperature cathode performance. NexTech's ultrasonic-spray deposition process was adapted for depositing both the interlayer and electrolyte films. Co-sintering methods were established for achieving flat multilayer cells comprised of a macro-porous LSM substrate, a micro-porous interlayer, and a dense YSZ electrolyte film (see Figure 1).

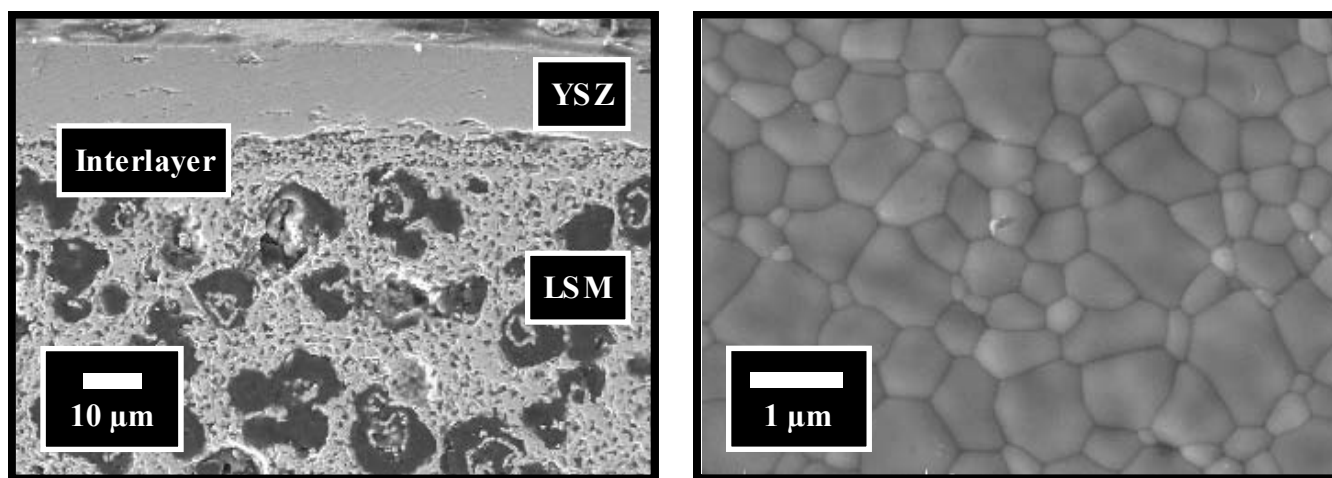


Figure 1. SEM micrographs of cathode-supported bilayer elements: polished cross-section (left) and electrolyte surface (right).

Ohio State University supported NexTech's process development work by using laser dilatometry to evaluate shrinkage during sintering, and optical profilometry to evaluate curvature in co-sintered elements (see Figure 2). During initial development, uncoated substrates and co-sintered elements exhibited considerable curvature. Optimization of processing reduced total curvature to less than 100 microns for co-sintered elements with 5-cm by 7-cm areas.

NexTech used its tape casting, ultrasonic-spray deposition and co-sintering methods to fabricate anode-supported elements with desired dense-electrolyte porous-anode morphology, as shown in Figure 3. The

fabrication of these anode-supported elements was scaled to 70-cm² areas (as required for long-term testing at GTI). ORNL developed a similar fabrication process, except that screen printing was used to deposit the YSZ electrolyte films. The advantage of ORNL's fabrication route is that the electrolyte coatings are deposited directly on the laminated anode substrate, without intermediate binder removal and heat treatment steps. ORNL's screen-printing process allows thickness of the YSZ electrolyte films (after sintering) to be controlled within the range of 10 to 30 microns. ORNL also developed processes for incorporating functional interlayers at the anode/electrolyte interface (see Figure 4).

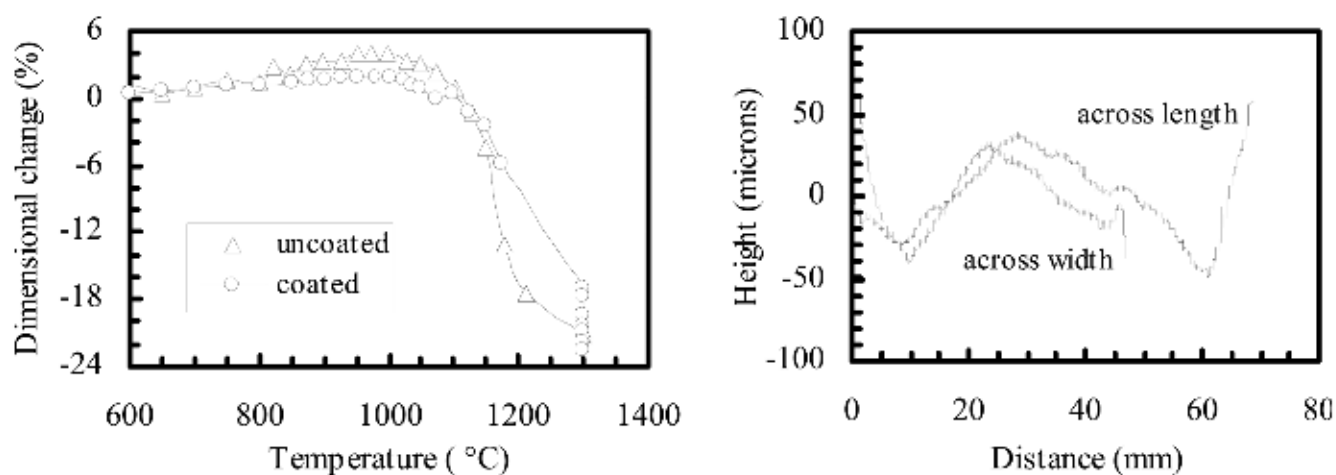


Figure 2. Sintering shrinkage of uncoated LSM substrate, and YSZ-coated substrate measured by laser dilatometry (left), and curvature of co-sintered cathode-supported bilayer element measured by optical profilometry (right).

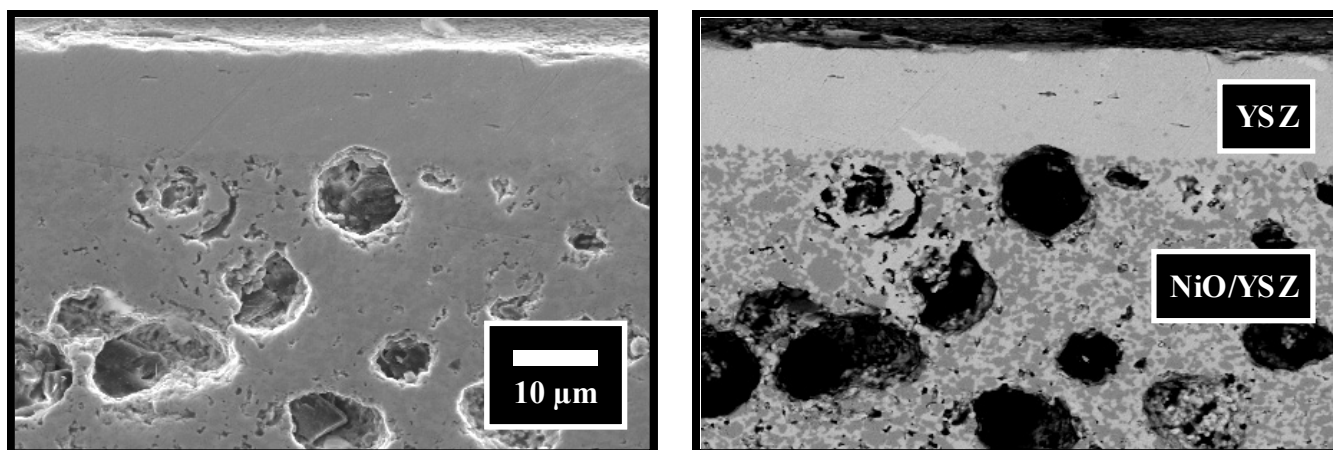


Figure 3. SEM micrograph of polished anode-supported element fabricated at NexTech (left), and corresponding BSE image showing distribution of nickel and YSZ in anode (left).

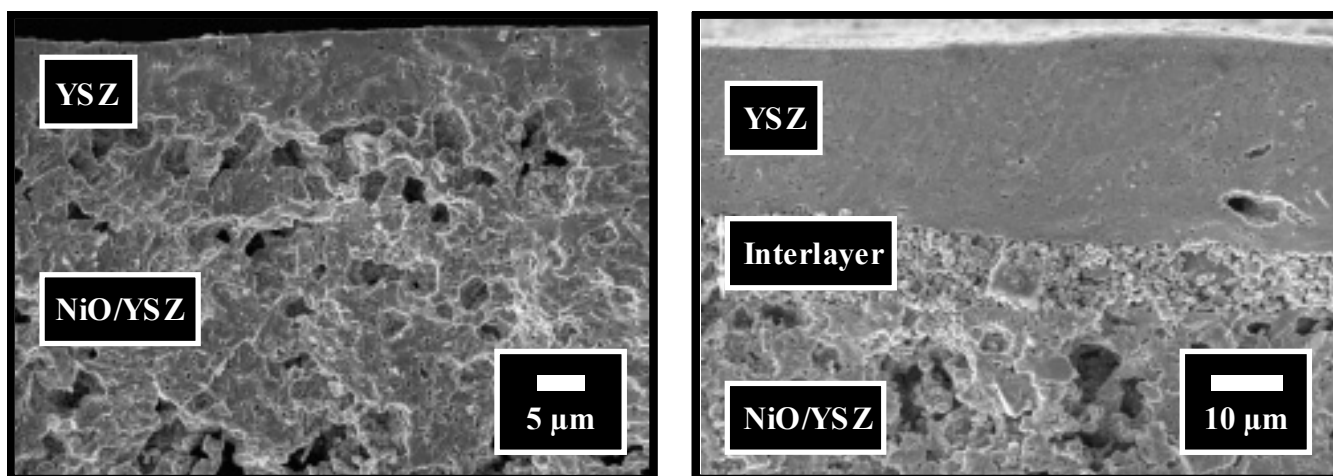


Figure 4. SEM micrographs of polished cross-sections of ORNL's anode-supported elements, without interlayer (left) and with a functional interlayer (right).

UMR's process for depositing ultra-thin YSZ electrolyte layers involves the initial preparation of a polymeric precursor solution (with cation stoichiometry of YSZ), followed by spin-coating YSZ layers onto a substrate. The primary advantage of UMR's process is that the nano-crystalline YSZ films produced by this process have extremely high ionic conductivity (more than 100 times that of coarse-grained YSZ). Successful integration of these electrolyte films in an SOFC will essentially eliminate all electrolyte resistance. The primary challenge associated with adapting UMR's spin-coating process to SOFC fabrication, is the need to fabricate a cathode

substrate that is sufficiently flat and smooth, and that has a fine-scale (sub-micron) surface porosity. Otherwise, the precursor solution will infiltrate into the substrate (or a multitude of spin-coating/annealing cycles will be required to achieve a dense and leak-tight electrolyte layer). The approach pursued by UMR was the initial deposition of a ceria-based interlayer to "planarize" the LSM surface by a colloidal process, followed by the deposition of YSZ films by spin-coating. With this strategy, UMR was able to demonstrate the fabrication of SOFC elements comprising ultra-thin, spin-coated electrolyte films on porous cathode substrates (see Figure 5).

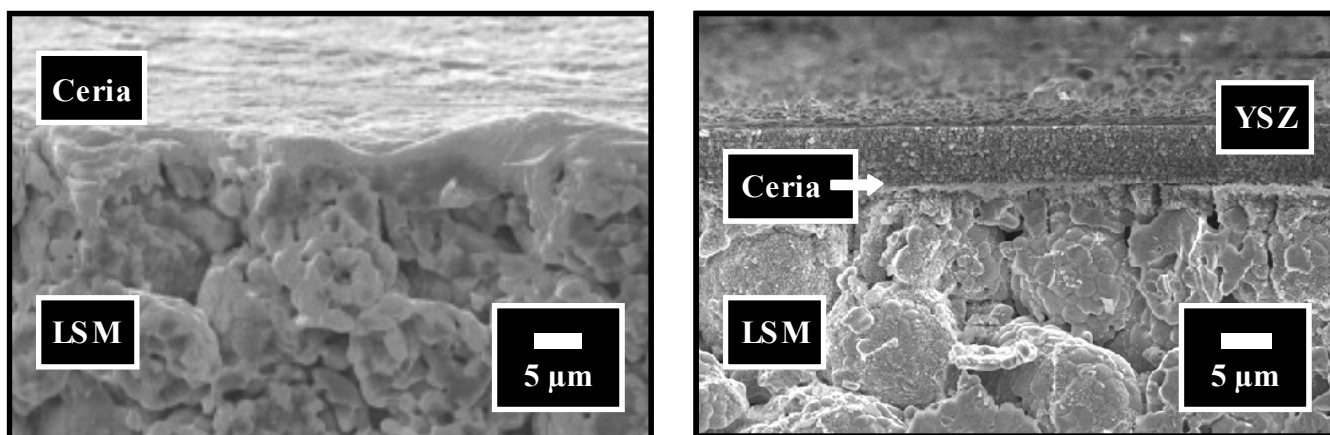


Figure 5. SEM micrographs showing a ceria interlayer on an LSM substrate (left), and the same structure with an YSZ film (right).

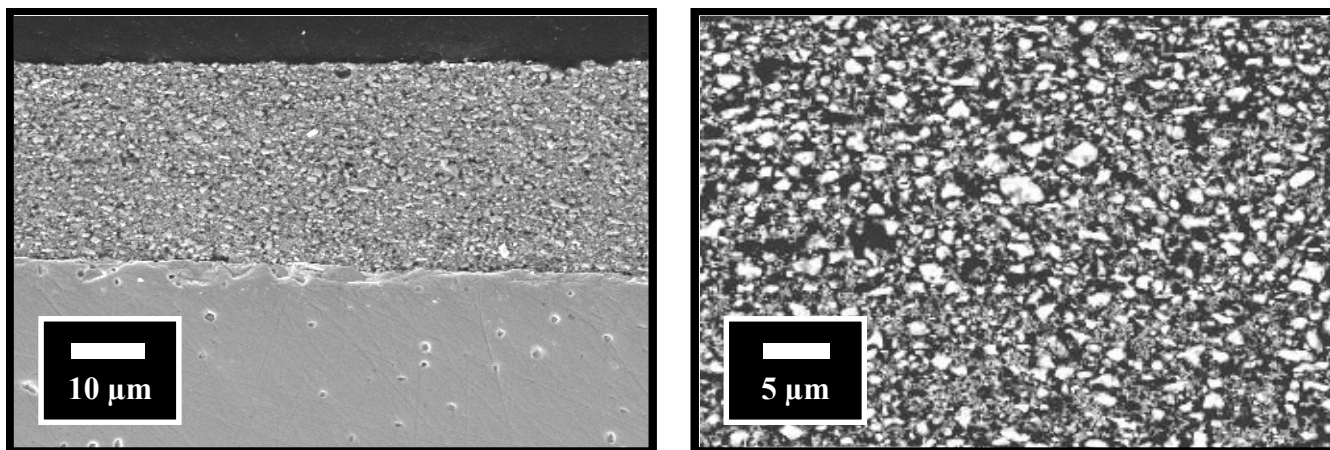


Figure 6. SEM and BSE micrographs of cross-sections of screen-printed composite (LSCF/GDC) cathode coatings.

NexTech developed a screen-printing process for preparing high-performance cathode materials based on nano-composite mixtures of perovskite electrode and gadolinium-doped ceria (GDC) electrolyte materials (see Figure 6). Lanthanum ferrite compositions were used as the perovskite component in the composite cathodes: $(\text{La}_{0.60}\text{Sr}_{0.40})\text{FeO}_3$ (LSF-40), $(\text{La}_{0.80}\text{Sr}_{0.20})\text{FeO}_3$ (LSF-20), and $(\text{La}_{0.60}\text{Sr}_{0.40})(\text{Fe}_{0.80}\text{Co}_{0.80})\text{O}_3$ (LSCF-6428). The electrolyte composition used in these cathodes was $(\text{Ce}_{0.90}\text{Gd}_{0.10})\text{O}_{1.95}$ (GDC-10). A relatively simple method was used to measure electrode resistivity: four-

point resistance measurements on GDC electrolyte ceramic discs with cathode coatings deposited onto both faces, and electrode resistivity was then calculated by subtracting the electrolyte resistance. Results of these tests are shown in Figure 7 for composite electrodes in the LSF-GDC and LSCF-GDC systems. Results of single-cell SOFC tests performed at Northwestern University on anode-supported cells prepared at NexTech and ORNL are presented in Figure 8. High performance ($>1 \text{ W/cm}^2$ at 800°C) has been achieved in anode-supported cells fabricated at NexTech and at ORNL.

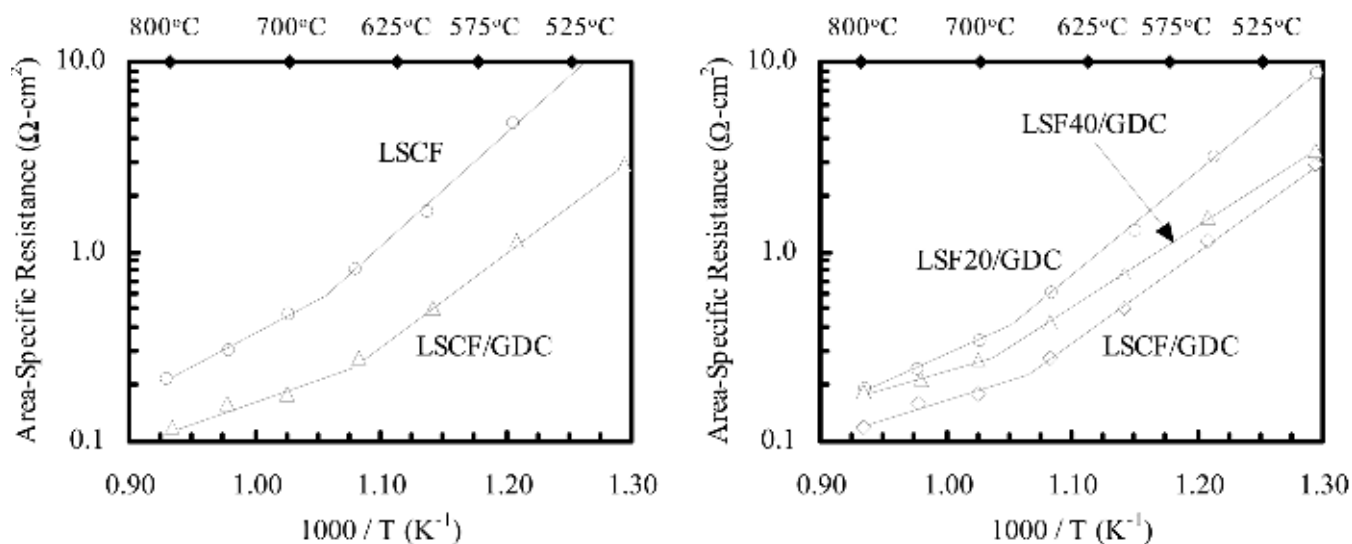


Figure 7. Arrhenius plots of electrode resistivity: comparison of LSCF and composite LSCF/GDC electrodes (left); and comparison of composite electrodes with different lanthanum ferrite-based compositions.

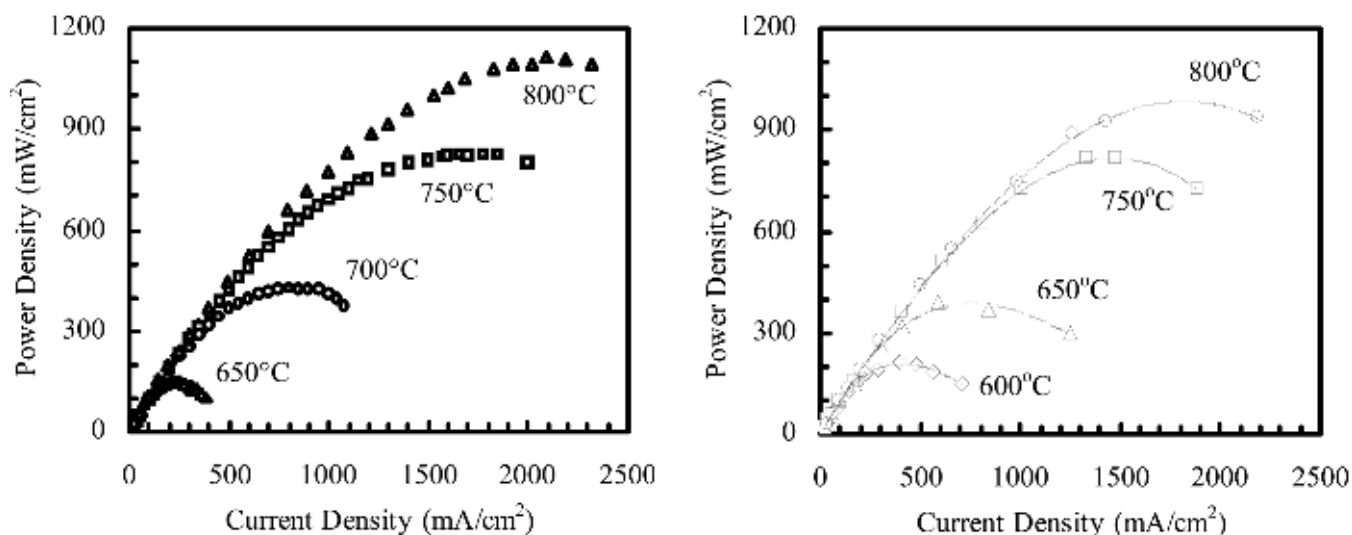


Figure 8. SOFC power density curves for anode-supported cells, measured at Northwestern University: NexTech anode-supported cell with composite LSF/GDC cathode (left); and ORNL anode-supported cell with LSCF/GDC cathode (right). These tests were conducted with hydrogen and air as reactants, with low utilization rates.

Conclusions

There are several important fabrication process variables that are critical to ultimate success in the high yield, low-cost manufacture of anode-supported solid oxide fuel cell elements with performance required for commercial applications. These include the following:

- Controlling green density and sintering shrinkage of anode substrates.
- Optimizing the tape casting and lamination processes to achieve ultimate uniformity of green density of anode substrates.
- Deposition of electrolyte films with high green density to minimize shrinkage and assure high sintered density.
- Optimizing co-sintering cycles to accommodate sintering shrinkage mismatches.
- Optimizing composition and processing of cathode materials, so that high performance can be retained when cathode coatings are applied by low-cost screen-printing methods.
- Performing critical fabrication operations in a clean environment.

One of the key challenges facing manufacturers of planar anode-supported SOFC elements is to achieve – at high volumes – required flatness specifications, without resorting to costly measures like constrained sintering and/or sinter forging. In this regard, laser dilatometry and optical profilometry have been established as valuable process development and non-destructive testing tools to address the flatness issue.

Current work in Phase III of this project involves comprehensive testing of anode-supported cells and the component materials used to make them. Single-cell SOFC testing at Northwestern focuses on the evaluation of several compositional and processing variables (anode formulations and processing, cathode formulations, etc.) on performance. In addition, long-term testing of large-area cells is being performed at GTI to provide application-specific data on how these cells will perform in stacks (i.e., with high fuel utilizations). A final ongoing project activity is mechanical property testing of anode and cathode substrates (in collaboration with Ohio State and ORNL).